

# Limitations on the Protective Action of MgSO<sub>4</sub> for Cellulose during Kraft Pulp Oxygen Delignification

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Magnesium sulfate (MgSO<sub>4</sub>) is the most widely used protector for alleviating the effects that metal ions have on cellulose degradation. However, the efficiency of MgSO<sub>4</sub> is limited by the oxygen delignification conditions. This work discusses the factors influencing MgSO<sub>4</sub> efficiency in terms of cellulose protection and delignification. The type and concentration of metal ions, delignification rate, additions order, and mixing degree of MgSO<sub>4</sub> should affect the cellulose degradation during oxygen delignification in the presence of MgSO<sub>4</sub>. The most adverse effects on cellulose are observed with Mn<sup>2+</sup> and Fe<sup>2+</sup> ions followed by Cu<sup>2+</sup> and Fe<sup>3+</sup>. MgSO<sub>4</sub> addition can diminish such negative effects; however the protection becomes reduced in the presence of higher concentrations of metal ions. In addition, the optimum MgSO<sub>4</sub> application level is closely dependent on the delignification rate and metal ions concentration. Adding MgSO<sub>4</sub> is optional for pulps with trace metal ions at relatively low delignification levels, but it is essential for pulps with concentrated metal ions or when the oxygen delignification rate is relatively high. More simply, when the added MgSO<sub>4</sub> is thoroughly mixed with the pulp before the addition of NaOH, it exhibits a prominent effect on cellulose protection.

*Keywords:* MgSO<sub>4</sub>; Oxygen delignification; Metal ions; Cellulose degradation

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## INTRODUCTION

Since it offers a way to avoid release of toxic chlorinated aromatic compounds, oxygen delignification has become widely popular. It is the most commonly used process in totally chlorine-free bleaching sequences because of its economic and ecological feasibility. The compatibility of the effluent from oxygen delignification with the kraft chemical recovery process, in addition to the reduction in the operating costs, have given the oxygen delignification process an advantage over other bleaching processes (McDonough 1995; van Heiningen *et al.* 2003; Bajpai 2005; van Heiningen *et al.* 2018). Oxygen delignification is typically conducted at moderate temperatures under an alkaline environment, where the oxygen reacts through complex radical chain reactions with both the lignin and carbohydrates. However, the delignification/cellulose degradation selectivity deteriorates in an oxygen delignification process at a higher delignification rate, or when the initial pulp exhibits a high kappa number (Tao *et al.* 2011; Jafari *et al.* 2014a). The poor selectivity is primarily due to the formation of hydroxyl radicals during oxygen delignification, and these can easily cleave the glycosidic bonds in cellulose *via* direct attack on the anomeric carbon (Guay *et al.* 2001; Guay *et al.* 2002). Transition metal ions in the pulp may facilitate the generation of highly reactive hydroxyl radicals, which in turn cause severe cellulose degradation (Gierer *et al.* 2001; Guay *et al.* 2001).

An effective approach to protect cellulose from degradation is therefore to control the generation of hydroxyl radicals in the oxygen delignification system. An effective method of removing transition metal ions from pulp is by washing the pulp with a chelating agent or mineral acid prior to oxygen delignification (Jones and Williams 2002; Granholm *et al.* 2009; Jafari *et al.* 2014b). However, considering the additional washing machinery and increase in caustic consumption, such technology is difficult to industrialize. Another excellent way to control the generation of hydroxyl radicals is by adding transition metal ion controllers or radical-scavenging biopolymers during the oxygen delignification process, *e.g.*, Na<sub>2</sub>EDTA (Zhao *et al.* 2018), zeolite (Hoang and Long 2017), chitosan (Li *et al.* 2015), guar-galactomannan (van Heiningen and Violette 2003), phenol (Chen and Lucia 2002), and anthraquinone (Liu *et al.* 2013). Among these approaches, the utilization of MgSO<sub>4</sub> is definitely the most effective relative to protecting cellulose from degradation. During oxygen delignification, the alkaline will cause MgSO<sub>4</sub> to be precipitated as Mg(OH)<sub>2</sub>, which can absorb transition metal ions or form complexes, thereby inhibiting peroxide decomposition. However, it is doubted that Mg<sup>2+</sup> can form a stable complex with carbonyl groups of cellulose to reduce the rate of cellulose degradation (Lapierre *et al.* 2003).

However, the protective benefits provided by the MgSO<sub>4</sub> protector to cellulose are limited. With the addition of the Mg protector, the degree of kappa reduction in a single oxygen delignification stage must be maintained at below 50% for softwood kraft pulps, to prevent excessive cellulose degradation and carbohydrate losses (van Heiningen *et al.* 2018). It has been found that an improper addition sequence of the Mg protector, *e.g.*, the addition of NaOH before MgSO<sub>4</sub> or the addition of insoluble Mg(OH)<sub>2</sub>, could also have a negative effect on cellulose protection (Bouchard *et al.* 2011). The proportion of metal ions to Mg is another important factor that affects the efficiency of Mg protection. According to Yokoyama *et al.* (1999), Mg<sup>2+</sup> displays the best protection effect on cellulose when the Mg<sup>2+</sup> to Mn<sup>2+</sup> ratio is greater than 30 mol/mol. Moreover, studies have revealed that the integration of MgSO<sub>4</sub> and other additives, *e.g.*, phenol (Fu *et al.* 2004) or EDTA (Lapierre *et al.* 2003), yields more effective cellulose protection. These studies have uncovered additional factors affecting the MgSO<sub>4</sub> efficiency, *e.g.*, metal ions and Mg<sup>2+</sup> addition methods; however, there has been a need to comprehensively evaluate these factors in terms of MgSO<sub>4</sub> efficiency.

To further enhance the performance of MgSO<sub>4</sub>, the authors continuing effort is to explore the factors influencing MgSO<sub>4</sub> efficiency in terms of cellulose protection in order to provide theoretical guidance for the efficient utilization of MgSO<sub>4</sub>. The present work, combined with various factor analyses, *e.g.*, transition metal ions in the pulp, delignification rates, chemical addition sequences, and pre-mixing, will provide a comprehensive analysis and evaluation of the factors which affect the MgSO<sub>4</sub> performance.

## EXPERIMENTAL

### Pulps

The pulps with different kappa numbers (KP-1, KP-2, KP-3, and KP-4) were self-made kraft pulps prepared in a laboratory. The KP-1 and KP-2 samples were prepared from *Eucalyptus grandis* × *urophylla*, while the KP-3 and KP-4 samples were prepared from *Pinus radiata* D. Don. The pulping experiment was carried out in a laboratory digester (M/K 609-2-10, M/K Systems, Williamstown, MA). The parameter information, namely

the active alkali (AA, expressed as Na<sub>2</sub>O), sulfidity, liquor to wood ratio, heating rate, and holding time are listed in Table 1. The kappa number, viscosity, and metal ion content of the above kraft pulp samples are listed in Table 2. NaOH and H<sub>2</sub>SO<sub>4</sub> were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. The MgSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>, MnSO<sub>4</sub>, CuSO<sub>4</sub>, and the chelating agent diethylenetriaminepentaacetic acid (DTPA) were purchased from Sinopharm Chemical Reagent Co. Ltd. The metal ion contents were determined *via* inductively coupled plasma mass spectrometry (ICP-MS) analysis. The detailed procedure was described in the authors previous work (Cao *et al.* 2014).

**Table 1.** Pulping Conditions of the Lab Kraft Pulp

| Pulp | AA (%) | Sulfidity (%) | Liquor to Wood Ratio | Cooking Temperature (°C) | Heating Rate (°C/h) | Holding Time (min) |
|------|--------|---------------|----------------------|--------------------------|---------------------|--------------------|
| KP-1 | 15     | 20            | 4:1                  | 160                      | 90                  | 90                 |
| KP-2 | 14     | 20            | 4:1                  | 160                      | 90                  | 90                 |
| KP-3 | 20     | 25            | 4:1                  | 170                      | 90                  | 60                 |
| KP-4 | 17     | 25            | 4:1                  | 170                      | 90                  | 60                 |

### Pulp Pre-treatment

The lab pulp was treated with DTPA and sulfuric acid in that sequence in order to remove the metal ions. The chelating treatment was conducted at a pH of 4, with a pulp consistency of 1% and an addition of 0.5% DTPA, for 60 min at 60 °C. After the chelating treatment, the pulp was treated with 2 mol/L sulfuric acid with a pH of 2. The other parameters were similar to those employed in the former chelating treatment. Subsequently, the pulp was washed several times with deionized water until the pH of the filtrate reached approximately 7. The residual metal ions in the pulps are shown in Table 2.

**Table 2.** Kappa Number, Viscosity, and Metal Ion Content of the Lab Kraft Pulp

| Pulp | Original Kappa | Viscosity (mL/g) | Metal Ion Content Before and After Sequential Acid Washing and Chelation Treatments (ppm) |       |                  |       |                  |       |                  |       |
|------|----------------|------------------|---|-------|------------------|-------|------------------|-------|------------------|-------|
|      |                |                  | Mg <sup>2+</sup>  |       | Fe <sup>3+</sup> |       | Mn <sup>2+</sup> |       | Cu <sup>2+</sup> |       |
|      |                |                  | Before  | After | Before           | After | Before           | After | Before           | After |
| KP-1 | 18.0           | 1063             | 248.0   | 5.3   | 14.1             | 12.1  | 2.0              | 0.4   | 0.8              | 0.3   |
| KP-2 | 22.7           | 1103             | 272.0   | 6.1   | 27.5             | 17.5  | 4.4              | 0.6   | 1.6              | 0.6   |
| KP-3 | 23.6           | 992              | 42.4  | 4.6   | 23.7             | 15.9  | 7.2              | 0.2   | 3.1              | 0.7   |
| KP-4 | 34.3           | 1094             | 66.1  | 4.1   | 37.5             | 22.8  | 6.4              | 0.1   | 1.9              | 0.5   |

### Introduction of Metal Ions

In order to investigate the effects of metal ions on cellulose degradation, the transition metal ions, *i.e.*, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, and Cu<sup>2+</sup> ions, were added to the treated pulp as required for oxygen delignification. In this case, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeSO<sub>4</sub>, MnSO<sub>4</sub>, and CuSO<sub>4</sub>

were added at 4 different concentrations (Table S1). Before adding the metal ions solutions, the pH of the kraft pulp slurry was adjusted to 2 by adding 0.1 mol/L H<sub>2</sub>SO<sub>4</sub>. After that, the pH of the pulp was adjusted to 9 with 0.1 mol/L NaOH in order to ensure the consistency of the alkali dosage, which was required for the subsequent oxygen delignification process.

### Chemical Addition

The following processes outline the chemical additions for the pulp samples:

NaOH process: did not include the addition of MgSO<sub>4</sub>.

MgSO<sub>4</sub> + NaOH process: First, MgSO<sub>4</sub> was added into the pulp and mixed for 2 min (hand kneading). After that, NaOH was added into the pulp slurry. Hand kneading was necessary for thoroughly mixing the chemicals and pulp.

NaOH + MgSO<sub>4</sub> process: First, NaOH was added into the pulp slurry, and after being mixed for 2 min, MgSO<sub>4</sub> was added and was hand kneaded before undergoing oxygen delignification.

Mg(OH)<sub>2</sub> + NaOH process: First, Mg(OH)<sub>2</sub> was added into the pulp and mixed for 2 min. After that, NaOH was added into the pulp slurry. Hand kneading was necessary for thoroughly mixing the chemicals and pulp.

MgSO<sub>4</sub> premixing process: Before undergoing oxygen delignification, the pulp slurry was mixed with MgSO<sub>4</sub> by stirring at 200 rpm for 60 min in order to thoroughly mix the pulp. The NaOH was added before the pulp underwent oxygen delignification.

### Oxygen Delignification

The oxygen delignification experiments were performed in a Parr autoclave (Parr 4577, Parr Instrument Co., Moline, IL, USA). Oxygen bleaching was conducted at a pulp consistency of 10% at 100 °C at an oxygen pressure of 1.0 MPa; the added NaOH and MgSO<sub>4</sub> contents were 4% and 0.5%, respectively. As required, the pulps with different kappa numbers and viscosities were obtained by delignifying the pulp for different time periods.

#### *Particle size analyses of Mg(OH)<sub>2</sub>*

To describe the effects of the MgSO<sub>4</sub> addition sequence on the properties of Mg(OH)<sub>2</sub>, and therefore oxygen delignification, Mg(OH)<sub>2</sub> was *in situ* formed from the reaction between MgSO<sub>4</sub> and NaOH with different addition sequences. The process in which MgSO<sub>4</sub> was added first is described as: NaOH with a concentration of 80 g/L (20 mL) was added drop-wise to 20 mL of MgSO<sub>4</sub> solution (2.4 g/L). By contrast, the process in which NaOH was added first is describe as: MgSO<sub>4</sub> with a concentration 2.4 g/L (20 mL), was added drop-wise to 20 mL of NaOH (80 g/mL) solution. For comparison, purchased Mg(OH)<sub>2</sub> powder was also used. The *in situ* produced and purchased Mg(OH)<sub>2</sub> suspension was then stirred for 1 h at 200 rpm. After that, the suspension was diluted several times to measure the particle size *via* a Malvern nanoparticle size analyzer (Malvern Instruments, Nano-ZS90, Malvern, UK) (Ning *et al.* 2019).

### Pulp Property Analysis

The kappa number and intrinsic viscosity of the pulp were determined in accordance with TAPPI test methods T236 om-13 (2013) and T230 om-13 (2013), respectively. The kappa number of the pulp was used to refer to the lignin content level, while the pulp viscosity was used to evaluate the level of cellulose degradation. While the

kappa number change was calculated by the following equation,

$$\text{kappa number change} = \frac{k_1 - k_0}{k_0} \times 100\% \quad (1)$$

where  $k_0$  is the kappa number of the pulp without the addition of  $\text{MgSO}_4$  and  $k_1$  is the kappa number of the pulp with the addition of  $\text{MgSO}_4$ . The viscosity increase was calculated by the following equation,

$$\text{viscosity increase} = \frac{v_1 - v_0}{v_0} \times 100\% \quad (2)$$

where,  $v_0$  is the viscosity of the pulp without the addition of  $\text{MgSO}_4$  and  $v_1$  is the viscosity of the pulp with the addition of  $\text{MgSO}_4$ .

## RESULTS AND DISCUSSION

### Transition Metal Type and Content Level

As shown in Figs. 1a and 1b, the effect of metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$  on lignin removal was marginal. It has been reported that metal ions, including  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{3+}$  can slightly promote delignification.  $\text{Cu}^{2+}$ , which acts as an electron acceptor, can accelerate the formation of phenoxy radicals, as well as the radical reaction, thus increasing the degradation rate of lignin.  $\text{Fe}^{3+}$  ions can form  $\text{Fe}^{3+}$ -complexes with phenolic compounds that link loosely to oxygen to form an  $\text{O}_2\text{-Fe}^{3+}$ -lignin intermediate, which catalyzes the degradation of lignin (Johansson and Ljunggren 1994; Wu and Heitz 1995). However, cellulose depolymerization, observed as a DP (degree of polymerization) drop, occurs with an increased intensity with the increase of metal ions concentration in pulp. In this case,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions are the most offensive ions, even at concentrations as low as 20 ppm, followed by  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions. Notably,  $\text{Fe}^{3+}$  has little effect on cellulose degradation. A carbohydrate model study revealed that in the presence of hydrogen peroxide,  $\text{Fe}^{2+}$  ions are the most harmful species to carbohydrates (Kishimoto and Nakatsubo 1998). In the oxygen delignification process, autoxidation leads to generation of the superoxide ( $\bullet\text{O}_2^-$ ) by electron transfer from the substrate to oxygen, demonstrated in Eq. 1.



The superoxide is the anionic form of the hydroperoxyl radical ( $\text{HO}_2\bullet$ ). Superoxide and the hydroperoxyl radical react at an almost diffusion-controlled rate giving oxygen and hydrogen peroxide (Gierer *et al.* 2001), as shown in Eq. 2,



The  $\text{Fe}^{2+}$  ions can catalyze the decomposition of  $\text{H}_2\text{O}_2$  molecules to form hydroxyl radicals, demonstrated in Eq. 3,



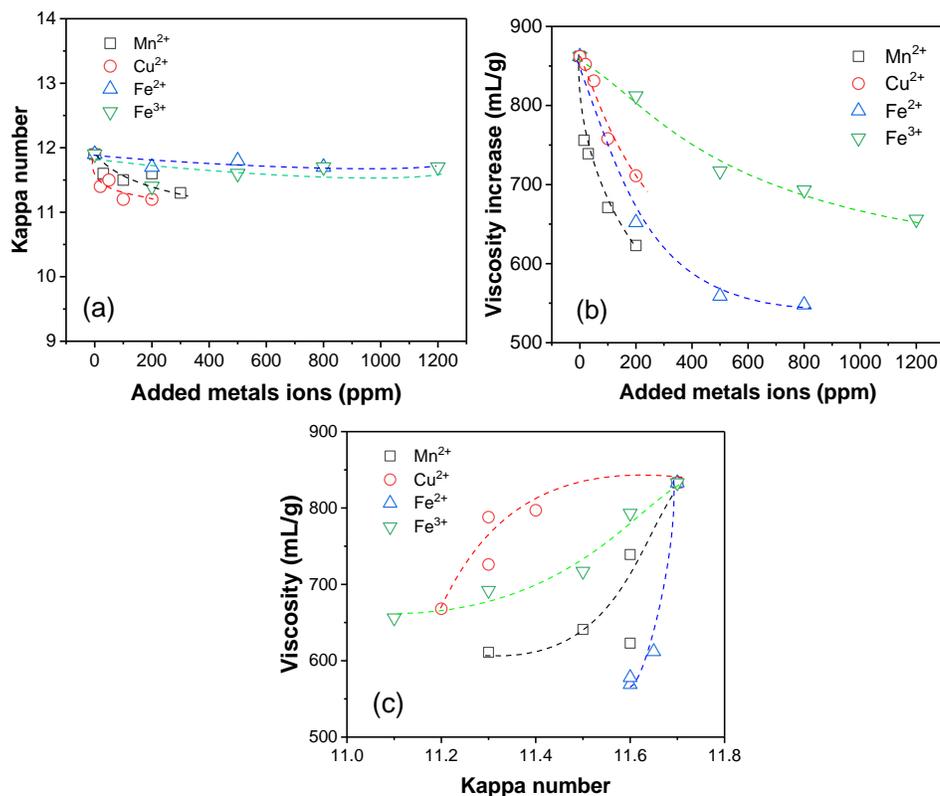
This is followed by the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions by hydrogen peroxide, demonstrated in Eq. 4 (Sixta *et al.* 2006),



The formation of hydroxyl radicals by the reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  ions is

inhibited as the  $\text{Fe}^{3+}$  concentration increases, and hence the impact of  $\text{Fe}^{3+}$  on cellulose degradation is small.

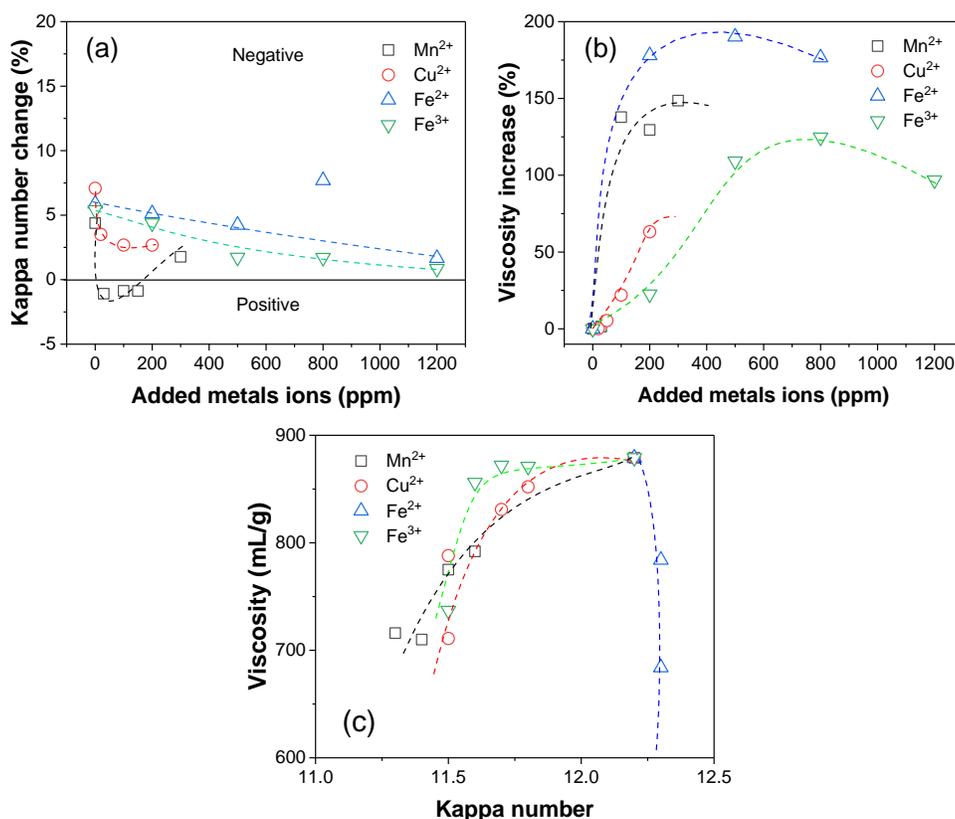
Figure 1c shows the correlation between the kappa number and the viscosity, and a high delignification selectivity was observed (selectivity is expressed as the ratio between viscose drop to kappa number change) in the presence of  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$ . In contrast,  $\text{Fe}^{2+}$  cannot promote delignification, but it can accelerate cellulose degradation.



**Fig. 1.** Effects of the metal ions on oxygen delignification (a) Kappa number; (b) cellulose viscosity; and (c) relationship between the Kappa number and viscosity. Eucalyptus (KP-1) pulp was used for the oxygen delignification in this experiment, which was subjected to sequential acid and chelating treatments prior to oxygen delignification.

Figure 2a suggests that the addition of  $\text{MgSO}_4$  can retard the delignification process. A positive kappa number change (defined as the ratio between the gain in the kappa number with the addition of  $\text{MgSO}_4$  to the kappa number of the pulp without the addition of  $\text{MgSO}_4$ ) is observed if the  $\text{Mn}^{2+}$  is out of consideration. However, the presence of  $\text{Mn}^{2+}$  ions can reduce the negative effect of  $\text{MgSO}_4$  on delignification. Figure 2b reveals that  $\text{MgSO}_4$  can effectively prevent the degradation of cellulose, but the protection effect of  $\text{MgSO}_4$  on cellulose is limited and varies with the metal concentration level and the metal type. Table S2 lists the viscosity loss per ppm of transition metal ions with and without the addition of  $\text{MgSO}_4$ . As the metal ion content increases, the viscosity loss per ppm of transition metal ions with and without the addition of  $\text{MgSO}_4$  tend to be similar. This means that the effect of the transition metal ions on cellulose degradation could not be reduced by adding  $\text{MgSO}_4$ , as the concentration of transition metal ions continued to increase. However,  $\text{MgSO}_4$  can significantly protect cellulose from degradation when the concentrations of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and

$\text{Cu}^{2+}$  are at low levels, according to the viscosity loss per ppm of transition metal ions with and without the addition of  $\text{MgSO}_4$ , or when  $\text{Fe}^{3+}$  concentrations are at high levels (up to 800 ppm) considering the value of viscosity (see Fig. S1). The  $\text{Mg}^{2+}$  ion exhibits a positive effect on cellulose protection. It has been proposed that at a pH of greater than 10, the  $\text{Mg}(\text{OH})_2$  precipitate formed from  $\text{MgSO}_4$  and an alkaline species can encapsulate  $\text{Mn}^{2+}$  ions to form a complex of variable composition  $(\text{Mg}_{1-x}\text{Mn}_x)(\text{OH})_2(\text{ss})$ , therefore effectively binding some of the transition metal ions (Lidén and Öhman 1998; Wiklund *et al.* 2001). This extra action between Mn and Mg might account for the significant effects observed. Moreover,  $\text{MgSO}_4$  is more efficient in eliminating cellulose degradation induced by  $\text{Fe}^{2+}$  ions, followed by the degradation induced by  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  ions, in descending order.



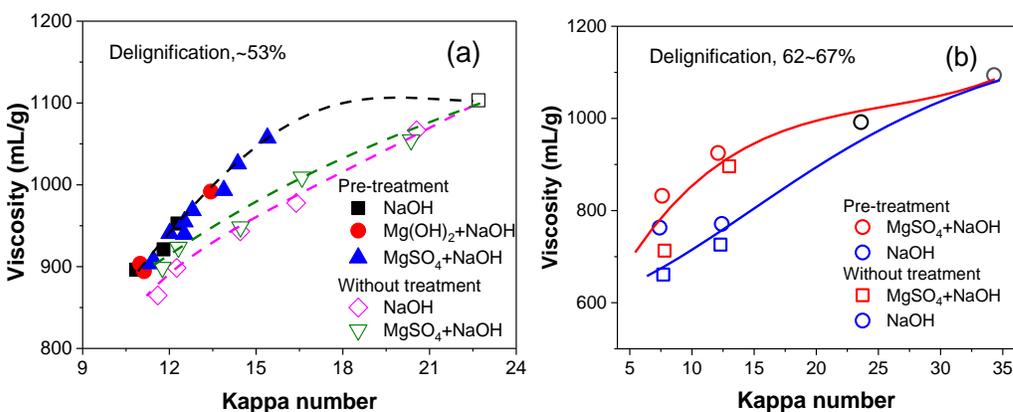
**Fig. 2.** Effect of  $\text{MgSO}_4$  on reducing the metal ion effects on oxygen delignification (a) Kappa number; (b) cellulose viscosity; and (c) relationship between the Kappa number and viscosity. Eucalyptus (KP-1) pulp was used in this experiment.

### Delignification Rate

Oxygen delignification is a competitive reaction between oxygen and oxygen species with residual lignin and carbohydrate. During this process, the accumulation of the condensed phenolics and p-hydroxyphenol units depends on the extent of oxygen delignification (Fu and Lucia 2003; Yang *et al.* 2003), and the functional units of lignin are resistant to further degradation. Therefore, as the oxidation resistance of lignin increases with the increase in the extent of oxygen delignification, the oxygen and oxygen species are more likely to react with carbohydrates than with lignin.

Figures 3a and 3b illustrate the Mg protection effects on oxygen delignification for

pulp at both high and low metal concentrations. As shown in Fig. 3a, when the starting pulp only contains a trace amount of metal ions, pre-treatment can remove most of the metal ions from the kraft pulp. Whether a Mg protector is added or how it is added has little effect on the cellulose degradation rate when the oxygen delignification is limited to less than 53%. It has been reported that an initial large Kappa loss is accompanied by a small loss in the cellulose viscosity, while a larger viscosity loss is observed at the end of the delignification process (van Heiningen *et al.* 2018).



**Fig. 3.** Selectivity at (a) relative low delignification (less than 53%); and (b) relative high delignification (62% to 67%). Pre-treatment involves sequential acid washing and chelation treatments. Without treatment means no pre-treatment. The KP-2 and KP-4 samples were used in this experiment.

When the pulp undergoes extensive oxygen delignification (greater than 60%), MgSO<sub>4</sub> is efficient in protecting cellulose from degradation in the metal ion-concentrated pulp. This protection is more significant in pulp with trace amounts of metal ions. The result is consistent with the Bouchard' study (2011) that the selectivity of oxygen delignification of the acid-washed pulp was improved when MgSO<sub>4</sub> is added prior to the oxygen stage.

### Addition Sequence

The data in Table 3 illustrates that the NaOH and MgSO<sub>4</sub> addition sequence has effects on oxygen delignification.

**Table 3.** Addition Sequence of the Chemicals

| Addition                   | Particle Size (d. nm) | Kappa Number | Viscosity (mL/g) |
|----------------------------|-----------------------|--------------|------------------|
| MgSO <sub>4</sub> + NaOH   | 850                   | 11.0 ± 0.5   | 792 ± 19         |
| NaOH + MgSO <sub>4</sub>   | 1206                  | 11.0 ± 0.0   | 777 ± 20         |
| NaOH                       | -                     | 10.5 ± 0.3   | 739 ± 18         |
| NaOH + Mg(OH) <sub>2</sub> | 2953                  | 11.0 ± 0.5   | 742 ± 17         |

Note: Eucalyptus pulp (KP-1) was used in this experiment, kappa number and viscosity are the values after oxygen delignification.

The addition of MgSO<sub>4</sub> prior to oxygen delignification has been shown to decrease the efficiency of the delignification process; under identical conditions, to provide pulp with a slightly higher kappa number than no Mg<sup>2+</sup> added (Kappa Number is 10.5 ± 0.3). In

contrast, the addition of  $\text{MgSO}_4$  has a positive influence on the viscosity of cellulose. In this case, the protection effect is independent of the amount of  $\text{MgSO}_4$  added and both  $\text{Mg}(\text{OH})_2$  and  $\text{MgSO}_4$  display a protection effect. However,  $\text{MgSO}_4$  is more effective than  $\text{Mg}(\text{OH})_2$ ; moreover, when  $\text{MgSO}_4$  is added before  $\text{NaOH}$  is added, it displays the most prominent protection effect, exhibited as the highest cellulose viscosity. The superior performance of  $\text{MgSO}_4$  over  $\text{Mg}(\text{OH})_2$  can be reasonably explained as the difference between the addition of soluble  $\text{Mg}^{2+}$  ions and insoluble  $\text{Mg}(\text{OH})_2$  molecules (Bouchard *et al.* 2011). The different size of the  $\text{Mg}(\text{OH})_2$  molecules, resulting from the various  $\text{MgSO}_4$  additions, could be one of the reasons. To investigate the effect of the chemical addition sequence on the size of  $\text{Mg}(\text{OH})_2$ , a controlled experiment was conducted in the presence of  $\text{MgSO}_4$  and  $\text{NaOH}$  with different addition sequences. A commercial  $\text{Mg}(\text{OH})_2$  sample was used for comparison. The size distribution of the  $\text{Mg}(\text{OH})_2$  colloidal particles is illustrated in Fig. 4, while the average sizes are listed in Table 3. The data revealed that the commercial  $\text{Mg}(\text{OH})_2$  sample presented a larger average size (2953 nm). When  $\text{MgSO}_4$  was added before  $\text{NaOH}$ , it was inclined to form small  $\text{Mg}(\text{OH})_2$  particles, which were smaller than those formed when  $\text{NaOH}$  is added first. The oxygen delignification process is usually conducted under alkaline conditions, which has a higher pH than the isoelectric point of the  $\text{Mg}(\text{OH})_2$  (pH of 12) in water. Accordingly, when  $\text{Mg}$  is added to  $\text{NaOH}$ , a pH value greater than 12 is reached in the reacting mixture. Therefore, the electric charge on the surface of the particles is expected to be negative, resulting in an extremely fast nucleation generation process (Song *et al.* 2011). Thus, the size of the  $\text{Mg}(\text{OH})_2$  particles formed by the  $\text{NaOH} + \text{MgSO}_4$  process were larger than those from the  $\text{MgSO}_4 + \text{NaOH}$  process. The small particle size of  $\text{Mg}(\text{OH})_2$  affords better performance of the adsorption properties of the transition metal ions, according to the adsorption mechanism of the  $\text{Mg}$  protector.

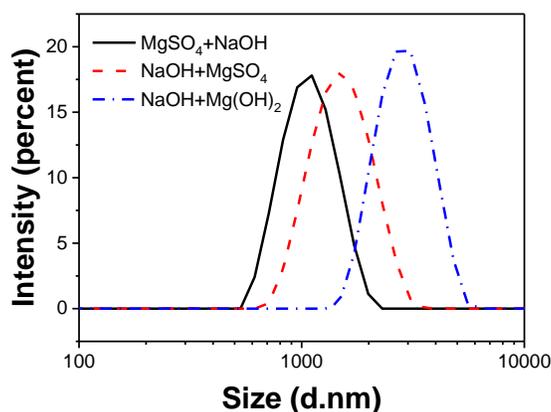


Fig. 4. Size of the  $\text{Mg}(\text{OH})_2$  colloidal particles based on the different chemical additions

### Pre-mixing

As mentioned in the above section, the prior addition of  $\text{MgSO}_4$  is important for the  $\text{Mg}^{2+}$  ions to be evenly distributed throughout the pulp fiber mixture. In this part of the study, thorough premixing was introduced prior to oxygen delignification and the resultant effects were investigated. The data in Table 4 revealed that premixing with  $\text{MgSO}_4$  significantly increased the cellulose viscosity for all of the pulp samples, confirming the importance of the uniform distribution of the  $\text{Mg}$  ions in the fiber suspension or cell walls. According to the Donnan equilibrium,  $\text{Mg}^{2+}$  ions can be effectively distributed in the pulp fiber suspension, fiber surface pores, and fiber cell cavities after reaching mass transfer

equilibrium. In this case, small-sized  $Mg(OH)_2$  molecules were synthesized *in-situ* with the addition of NaOH; this is beneficial for cellulose protection. It has been proposed that the Mg ions is a prerequisite for effective physical encapsulation of the transition metal hydroxides within the  $Mg(OH)_2$  precipitate when NaOH is added (Bouchard *et al.* 2011); where, the Mg ions can complex with the carboxylic acids and carbonyl groups present in the cellulose, thus preventing cellulose degradation. In all, it is demonstrated that the thorough mixing of the  $MgSO_4$  and pulp can help cellulose from degradation. Compared to the other factors such as metal ions, delignification rate, addition order of the chemicals, premixing procedure is readily to be achieved as “ $MgSO_4$  added before NaOH process” in a pulp mill.

**Table 4.** Comparison of the Performance of Oxygen Delignification between the Process With and Without Pre-mixing of  $MgSO_4$

| Pulps | Performance      | Original Pulp |                  |           | Prior Treatment |                  |           | Pulp with Metal Ions |                  |           |
|-------|------------------|---------------|------------------|-----------|-----------------|------------------|-----------|----------------------|------------------|-----------|
|       |                  | NaOH          | Mg <sup>2+</sup> | Premixing | NaOH            | Mg <sup>2+</sup> | Premixing | NaOH                 | Mg <sup>2+</sup> | Premixing |
| KP-3  | Kappa            | 12.3          | 13.0             | 15.4      | 12.4            | 12.1             | 12.3      | 10.3                 | 10.6             | 10.9      |
|       | Viscosity (mL/g) | 726           | 896              | 941       | 771             | 925              | 949       | 447                  | 571              | 629       |
|       | Selectivity      | 1.9           | 3.4              | 4.3       | 2.2             | 4.2              | 4.8       | 1.2                  | 1.4              | 1.7       |
| KP-2  | Kappa            | 7.7           | 7.8              | 7.3       | 7.4             | 7.6              | 7.3       | 6.4                  | 6.7              | 7.1       |
|       | Viscosity (mL/g) | 661           | 713              | 741       | 763             | 832              | 849       | 509                  | 511              | 548       |
|       | Selectivity      | 2.4           | 3.0              | 3.5       | 4.0             | 6.9              | 8.7       | 1.6                  | 1.6              | 1.7       |
| KP-1  | Kappa            | -             | -                | -         | 7.9             | 8.1              | 8.3       | 7.0                  | 7.8              | 7.9       |
|       | Viscosity (mL/g) | -             | -                | -         | 733             | 815              | 842       | 532                  | 560              | 591       |
|       | Selectivity      | -             | -                | -         | 2.0             | 2.7              | 3.0       | 1.3                  | 1.2              | 1.3       |

Note: Pulp with metals contents (Mn: 100 ppm, Cu: 100 ppm, Fe(II): 200 ppm, Fe(III):500 ppm). NaOH indicates the oxygen delignification was under alkaline conditions only; Mg<sup>2+</sup> indicates  $MgSO_4$  + NaOH process; and premixing indicates  $MgSO_4$  premixing process.

## CONCLUSIONS

1. The efficiency of  $MgSO_4$  in terms of cellulose protection during oxygen delignification varied with the types and levels of the metal ions, delignification rates, pre-mixing, and addition sequence of the chemicals.
2.  $MgSO_4$  was most effective in eliminating the cellulose degradation resulting from  $Fe^{2+}$ , but exhibited a feeble influence relative to the detrimental effects of other metals.
3. The addition of  $MgSO_4$  is optional for the pulps with prior acid washing and EDTA chelation at relatively low delignification rates (<53%), but it is essential for pulps with higher concentration of metal ions independent of the extent of delignification.
4. The addition order of  $MgSO_4$  and NaOH showed more influence on cellulose degradation than delignification.  $MgSO_4$  added before NaOH process was demonstrated to be effective for cellulose protection.
5. Thorough mixing of  $MgSO_4$  and the pulp helps protect cellulose from degradation and is readily incorporated into industrial processes.

## CONFLICTS OF INTEREST

The authors declare no competing financial interest.

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## APPENDIX

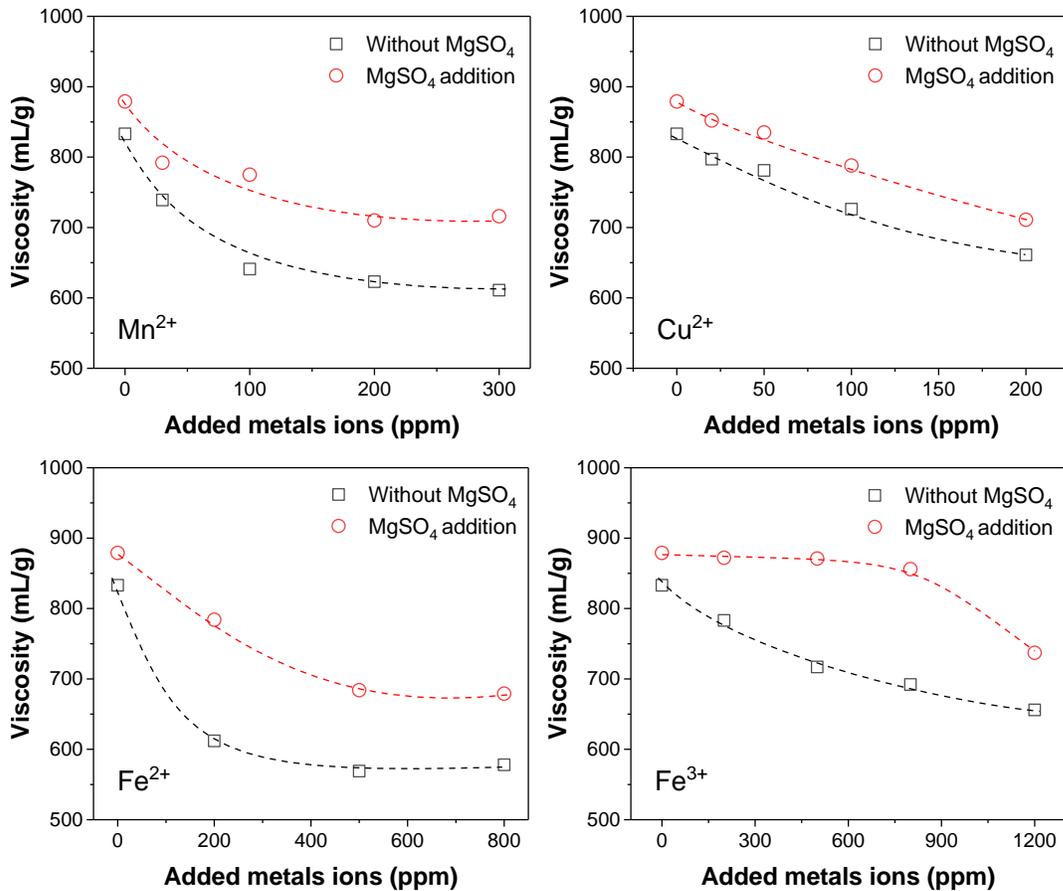
## Supplemental Information

**Table S1.** Addition Amount of Transition Metal Ions

| Metal ions       | Addition amount (ppm) |         |         |         |         |
|------------------|-----------------------|---------|---------|---------|---------|
|                  | Control               | Level 1 | Level 2 | Level 3 | Level 4 |
| Fe <sup>3+</sup> | 0                     | 200     | 500     | 800     | 1200    |
| Fe <sup>2+</sup> | 0                     | 200     | 500     | 800     | 1200    |
| Mn <sup>2+</sup> | 0                     | 15      | 30      | 100     | 200     |
| Cu <sup>2+</sup> | 0                     | 20      | 50      | 100     | 200     |

**Table S2.** Viscosity Loss Brought by per ppm Transition Metal Ions

| Metal Ions       | MgSO <sub>4</sub> addition | Viscosity Loss Brought by per ppm transition Metal Ions |            |           |           |
|------------------|----------------------------|---|------------|-----------|-----------|
|                  |                            | <Level 1  | Level 1~ 2 | Level 2~3 | Level 3~4 |
| Mn <sup>2+</sup> | /                          | 3.37  | 1.40       | 0.18      | 0.12      |
|                  | Addition                   | 2.43  | 0.24       | 0.65      | 0.06      |
| Cu <sup>2+</sup> | /                          | 1.65  | 0.30       | 1.24      | 0.58      |
|                  | Addition                   | 0.50  | 0.70       | 0.86      | 0.77      |
| Fe <sup>2+</sup> | /                          | 1.09  | 0.14       | 0.03      | /         |
|                  | Addition                   | 0.36  | 0.33       | 0.02      | /         |
| Fe <sup>3+</sup> | /                          | 0.20  | 0.25       | 0.08      | 0.09      |
|                  | Addition                   | 0.07  | 0.07       | 0.05      | 0.30      |



**Fig. S1.** Effect of MgSO<sub>4</sub> addition on viscosity under different kinds and levels of transition metal ions. Eucalyptus (KP-1) pulp is employed for oxygen delignification in this experiment, which is subjected to sequential acid and chelating treatments prior to oxygen delignification.